

Electronic states in 1/1 Cd₆Yb and 1/1 Cd₆Ca: Relativistic, correlation, and structural effects

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The electronic structure of the rational approximants 1/1 Cd₆Yb and 1/1 Cd₆Ca to the stable icosahedral CdYb and CdCa quasicrystals is studied by the full-potential linear augmented plane wave method. A comparison is made between several structural models. We show that the (relativistic) spin-orbit (SO) interaction and electronic correlations that are not described by the usual local density approximation, are essential for an accurate description of the electronic structure. In particular, we show that the SO interaction is responsible for a splitting of the Cd-4*d* and Yb-4*f* peaks, and that the experimental peak positions can be reproduced by including a Hubbard *U* term in the Hamiltonian [*U*(Cd) = 5.6 eV, *U*(Yb) = 3.1 eV]. Our results show very good agreement with a photo-emission (PE) spectrum of 1/1 Cd₆Yb [R. Tamura, Y. Murao, S. Takeuchi, T. Kiss, T. Yokoya, and S. Shin, Phys. Rev. B **65**, 224207 (2002)] and a 350 eV PE spectrum of 1/1 Cd₆Ca, which we present in this paper. Without the relativistic and correlation effects even a qualitative agreement with the PE spectra cannot be achieved.

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The recently discovered binary icosahedral quasicrystals (QCs) *i*-CdYb¹ and *i*-CdCa² have received considerable attention. Their electronic structures have been calculated and analyzed³ from the viewpoint of their stability and differences with respect to ternary Al-based QCs. The purpose of this communication is to point out that two elements ignored in previously published calculations, namely, the spin-orbit (SO) coupling and correlation effects, are of crucial importance for an accurate description of the electronic structure of these QCs. In addition, this communication addresses the issue of the stability of various structural models proposed for the 1/1 approximants of these QCs.

The binary icosahedral QCs *i*-CdYb and *i*-CdCa were discovered^{1,2} in 2000. Prior to this discovery the most studied QCs were the ternary alloys *i*-AlCuFe, *i*-AlPdMn, *i*-AlPdRe, *d*-AlNiCo, and *d*-AlCuCo. It has been anticipated¹ that binary QCs simplify the analysis of experimental properties. The study of *i*-CdYb and *i*-CdCa has indeed shed light on properties that are arguably still not well understood in the above-mentioned ternary QCs, such as the negative temperature coefficient of the resistivity⁴ and the origin of the pseudogap in the electronic density of states (DOS).^{3,5}

Theoretically the binary QCs require a more sophisticated approach than the above-mentioned ternary QCs because of the relatively heavy elements they contain: As we will show, the (relativistic) SO interaction and electron-electron interactions that are not described by the usual local density approximation (LDA), cannot be ignored. Because these effects are most prominent in *i*-CdYb, we will focus on this QC.

1/1 Cd₆Yb⁶ is a rational approximant⁷ to *i*-CdYb. Its structure can be described⁸ as a bcc packing of interpenetrating icosahedral clusters (Fig. 1). *i*-CdYb is composed of the same clusters.^{9,10} Whereas the exact structure of *i*-CdYb has not been determined, the structure of 1/1 Cd₆Yb is known. Some uncertainty exists only about the positions of the four Cd atoms inside the so-called dodecahedral cavity (Fig. 1).

1/1 Cd₆Ca is isostructural with 1/1 Cd₆Yb: Ca atoms replace Yb. In this paper we present an *ab initio* electronic structure study of 1/1 Cd₆Yb and 1/1 Cd₆Ca. Because of the structural proximity of the binary icosahedral QCs and their 1/1 approximants we expect that our results that do not depend on the long-range order of these materials, are also valid for *i*-CdYb and *i*-CdCa.

We studied 1/1 Cd₆Yb and 1/1 Cd₆Ca with the computer program WIEN2k,¹¹ an implementation of the full-potential linear augmented plane-wave method¹² based on density functional theory.¹³ For the exchange and correlation potential we used the LDA.¹⁴ In our DOS calculations we included the SO coupling using the so-called “second variational treatment.”¹⁵

Although the LDA gives reliable optimal atomic positions for many materials, for the same materials it may fail to predict the proper electronic ground state.¹⁶ In particular, the LDA description of the electronic structure of compounds containing (strongly correlated) transition-metal *d* or rare-earth *f* electrons is often inadequate.¹⁷ As we will show below, a good example of this shortcoming of the LDA is the wrong prediction³ for the position of the Yb-4*f* states in the DOS of 1/1 Cd₆Yb. A qualitative improvement is achieved by the LDA + *U* method,¹⁸ which takes into account the orbital dependence of the Coulomb and exchange interactions, which is absent in the LDA.¹⁷

We applied the LDA + *U* formalism of Ref. 18 to the Cd-4*d* and the Yb-4*f* states. The orbital potentials felt by these states depend on two adjustable parameters: the Coulomb parameter *U* (also called Hubbard *U*) and the exchange parameter *J*. For fully occupied orbitals like the Cd-4*d* and the Yb-4*f* states in 1/1 Cd₆Yb it is straightforward to show that the effect of *U* and *J* is to shift the orbital potential by $-\frac{1}{2}(U - J)$. Therefore we could choose *J* = 0 without loss of generality. We adjusted *U* to find the best possible agreement with a photo-emission (PE) spectrum of Ref. 19 and a PE spectrum that we present in this paper. Our optimal values are *U*(Cd) = 5.6 and

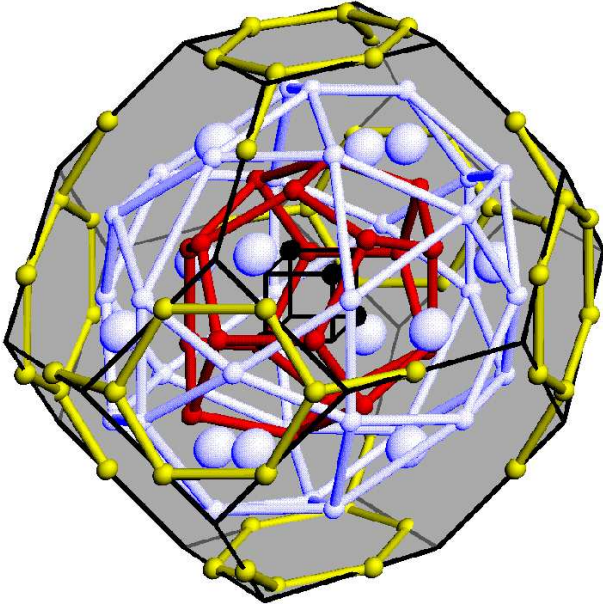


FIG. 1: (Color online) Unit cell of 1/1 Cd_6Yb (spacegroup $I23$). The Cd (small) and Yb atoms (large) form a shell structure. In the center Cd atoms are located on four vertices of a cube. The next shell (the dodecahedral cavity) consists of Cd atoms placed on the vertices of a dodecahedron. The third shell is a Cd icosidodecahedron composed of triangles and pentagons. Yb atoms are located at the centers of the pentagons. The remaining Cd atoms and Cd atoms of the icosidodecahedra in neighboring unit cells (not shown) form a defect triacontahedron (Ref. 8).

$$U(\text{Yb}) = 3.1 \text{ eV}$$

Different structural models have been proposed for 1/1 Cd_6Yb . They differ essentially only in the positions of the four Cd atoms inside the dodecahedral cavity (Fig. 1). Structural details are often important for the electronic structure. Therefore we made a comparison of the various structural models. In the original model⁶ of 1/1 Cd_6Yb the Yb and Cd atoms are on the same positions (scaled by the lattice parameter a) as Ru and Be in $\text{Ru}_3\text{Be}_{17}$ (Ref. 20). Four additional Cd atoms are located⁶ on four vertices of a cube [Fig. 2(a)] inside the dodecahedral cavity. The spacegroup of this original model is $I23$ (Ref. 6).

To calculate a good electronic DOS it is in general necessary to use accurate atomic positions.^{21,22,23} In particular, idealized positions may lead to a DOS with unphysical features (spikes),²¹ a pseudogap at the Fermi energy E_F that is too narrow,²¹ or shifted peaks.²² Therefore we have performed²³ a structural relaxation of the atomic positions of the original model of 1/1 Cd_6Yb . Our final positions²³ are relatively close to the original positions.⁶ During the structural relaxation the total energy decreased by 17 meV / atom. In the DOS the peak around $E_F - 9$ eV became 14 % narrower [Figs. 3(a) and 3(b)], indicating a reduced (spatial) overlap of the Cd-4d states.

Use of the generalized gradient approximation²⁴ (instead of the LDA) resulted in marginally different atomic positions. The main changes in the DOS were a lowering of the Cd-4d

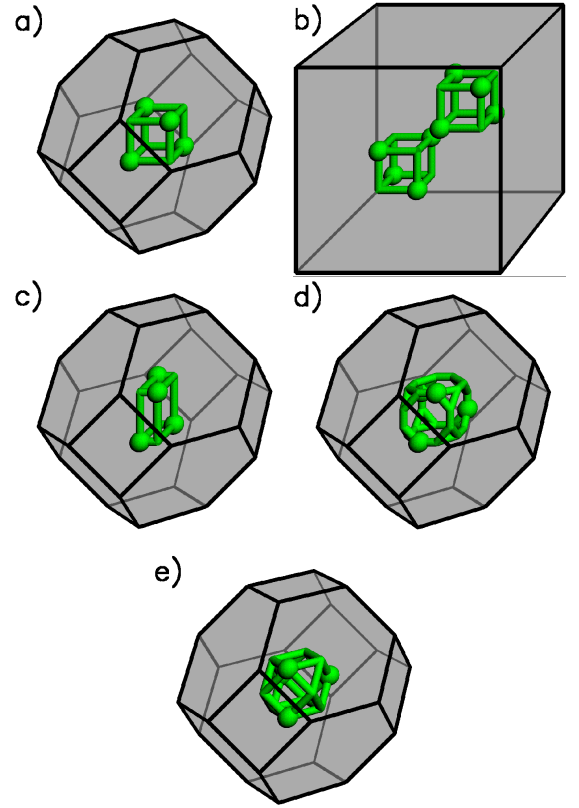


FIG. 2: (Color online) Models of 1/1 Cd_6Yb differ from each other in the positions of the Cd atoms inside the dodecahedral cavity (Fig. 1). These positions and the unit cells are schematically indicated for models with symmetries (a) $I23$, (b) $\text{Pn}\bar{3}$, (c) $I222$, (d) $C2$, and (e) $\text{Imm}2$ (See text).

states by 0.06 eV and an increase of the Yb-4f peak by 0.01 eV. In the present study we are not interested in such small differences. Therefore, we present results for the LDA only.

Electrical resistivity, specific heat, and electron diffraction experiments have suggested²⁵ that at low temperatures ($T < 110$ K) a structure with a simple cubic unit cell (space-group $\text{Pn}\bar{3}$) is favored over the bcc $I23$ structure. (Later experiments²⁶ have indicated that the low-temperature phase is noncubic, but for computational reasons we will consider noncubic structures only in the body-centered models.) In the $\text{Pn}\bar{3}$ model the Cd atoms inside the dodecahedral cavities occupy vertices of cubes with an alternating orientation [Fig. 2(b)]. The DOSs of the original $I23$ and $\text{Pn}\bar{3}$ models are not significantly different.²⁷ We relaxed the $\text{Pn}\bar{3}$ model. The total energy of the relaxed $\text{Pn}\bar{3}$ model was 0.4 meV / atom lower than that of the relaxed $I23$ model. Further convergence studies would be necessary to establish whether this number is significant. For the present study, however, it suffices to say that we found that the DOSs of the relaxed $I23$ and $\text{Pn}\bar{3}$ models were practically identical, and that we therefore restricted ourselves to the computationally less involved body centered models, such as the $I23$ model [Fig. 2(a)].

Another modification of the $I23$ model has been proposed on the basis of a recent x-ray diffraction study.⁸ According to

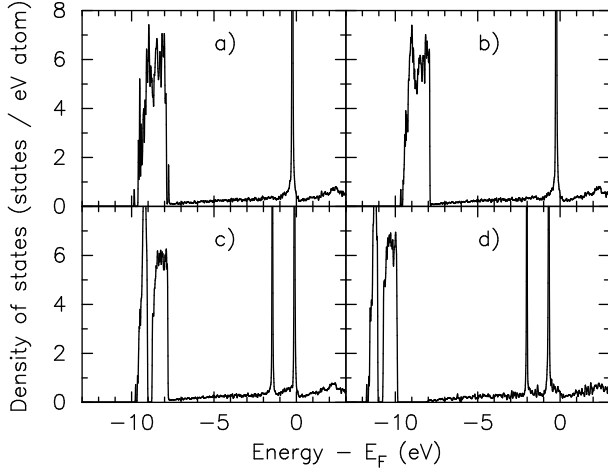


FIG. 3: Electronic DOS of 1/1 Cd_6Yb (spacegroup I23). (a) Original model (Ref. 6). (b)–(d) Relaxed model (Ref. 23). In (c) and (d) the SO interaction is included. (d) was calculated with the LDA + U method. All DOSs were convoluted with a Gaussian with a full width at half maximum of 30 meV. The DOS in (d) is not as smooth as the other DOSs, because fewer \mathbf{k} points were used to calculate it.

this study the central Cd atoms are located on vertices of a truncated cube [Fig. 2(d)]. When we tried to occupy four of these vertices, we found that there are only two inequivalent ways to do this (we discarded Cd-Cd nearest neighbor distances that were shorter than 2.4 Å). The first possibility is that the Cd atoms are on vertices of a rectangular parallelepiped [Fig. 2(c)]. This structure has spacegroup I222. When we relaxed these atomic positions we found that the atoms moved to the positions corresponding to the I23 symmetry [Fig. 2(a)], indicating that the I222 structure is not stable. The second possibility is indicated in Fig. 2(d). The spacegroup is C2. When we relaxed the atomic coordinates of this model we found that the Cd atoms moved to positions somewhere in between vertices of a cube octahedron [Fig. 2(e)] and vertices of an icosahedron. The spacegroup of this model is Imm2. The Imm2 model had a total energy that was 2 meV / atom lower than that of the relaxed I23 model, indicating that the Imm2 structure is more stable than the I23 structure. The peak positions in the DOSs of the relaxed Imm2 and I23 models were equal within 0.01 eV.

Summarizing our results so far, we found that the different models of 1/1 Cd_6Yb had similar electronic DOSs. The only significant change was a narrowing of the Cd-4d peak after the structural relaxation of the original I23 model. It is of particular interest that the main features in the DOS were found to be insensitive to the precise positions of the four Cd atoms inside the dodecahedral cavity, which is consistent with the theoretical result of Ref. 27 that these Cd atoms are weakly bound and do not play an important role in stabilizing 1/1 Cd_6Yb . In the rest of this paper we present results for the model with the highest symmetry, i.e., the I23 model.

We calculated the electronic DOSs of 1/1 Cd_6Yb and 1/1 Cd_6Ca . A separate structural relaxation was performed for 1/1 Cd_6Ca . Figure 3 shows our results for 1/1 Cd_6Yb obtained at various levels of sophistication. The result of Fig. 3(a) was

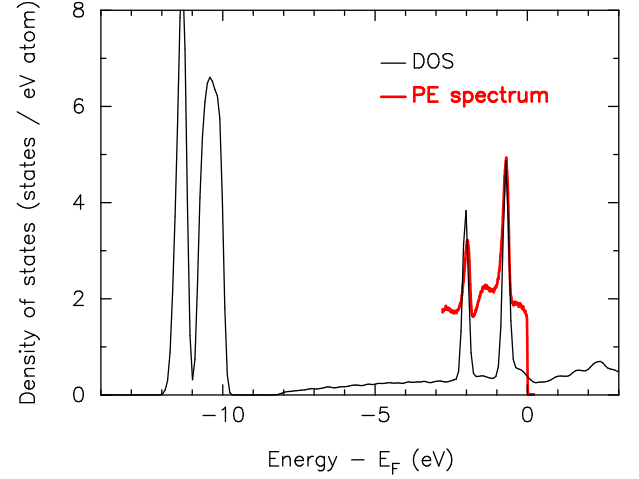


FIG. 4: (Color online) Comparison of the calculated DOS of 1/1 Cd_6Yb with a PE spectrum (Ref. 19). The DOS was convoluted with a Gaussian with a full width at half maximum of 200 meV.

obtained without SO coupling or orbital potentials (Hubbard U s) for the original I23 model. It is essentially equal to the result of Ref. 3. The main features are the Cd-4d peak around $E_F - 9$ eV, one Yb-4f peak just below the Fermi energy, and a pseudogap near E_F . In Ref. 3 it has been shown that this stabilizing pseudogap is formed as a consequence of hybridization between the free-electronlike s and p states and low-lying (unoccupied) Yb-5d states.

The DOSs of Ref. 3 and Fig. 3(a) are in disagreement with a PE spectrum¹⁹ of 1/1 Cd_6Yb , in which there are two Yb-4f peaks around 2.0 and 0.7 eV below the Fermi energy. The 1.3 eV split between these peaks is attributed¹⁹ to the SO interaction. It has been suggested¹⁹ that differences between the Yb-4f peak positions in the DOS of Ref. 3 and in the PE spectrum of Ref. 19 are due to a shape approximation for the potential that has been made in Ref. 3. The fact that our full-potential calculation is essentially equal to the result of Ref. 3 shows that this is wrong. In fact, a comparison of Figs. 3(b) and 3(c) shows that the most obvious discrepancy between Fig. 3(a) and the experiment,¹⁹ namely, the absence of the SO splitting in Fig. 3(a), is a result of the absence of the SO interaction in the calculation.

As mentioned above the structural relaxation of the I23 model of 1/1 Cd_6Yb led to a narrowing of the Cd-4d peak [Figs. 3(a) and 3(b)]. The SO interaction split the Yb-4f and Cd-4d peaks [Fig. 3(c)]. By including a Hubbard- U term in the Hamiltonian for the Cd-4d and Yb-4f states we could shift these peaks to lower energies [Fig. 3(d)]. We adjusted the U s to get the best possible fit with the PE spectra shown in Figs. 4 and 5. Our final DOSs reproduced the experimental peak positions very well (Figs. 4 and 5).

The PE spectrum of 1/1 Cd_6Ca (Fig. 5) was measured by x-ray PE spectroscopy with an incident photon energy of 350 eV at the temperature of 20 K using a GAMMADATA-SICENTA SES2002 hemispherical analyzer. Details of the sample preparation have been given elsewhere.⁵ The Cd-4d states are greatly enhanced in the experimental spectrum since

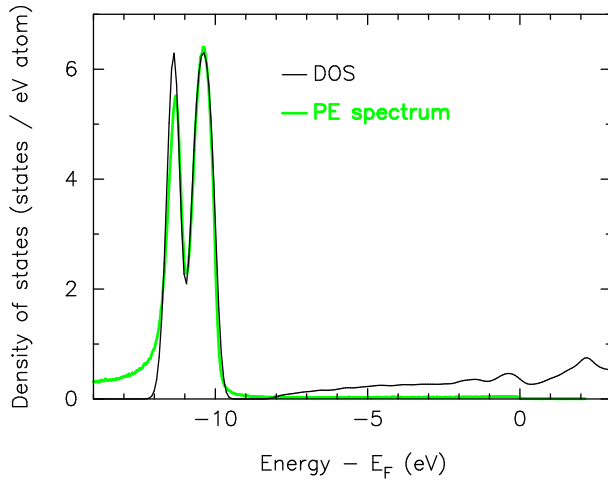


FIG. 5: (Color online) Comparison of the calculated DOS of 1/1 Cd_6Ca with a PE spectrum (See text). The DOS was convoluted with a Gaussian with a full width at half maximum of 400 meV.

TABLE I: Calculated and measured electronic contributions to the specific heat. The values are given per “mole formula unit”, viz., Cd_6Yb and $\text{Cd}_{5.7}\text{Yb}$ for the 1/1 approximant and the QC, respectively.

Calculation / Experiment	γ ($\text{mJ mol}^{-1} \text{K}^{-2}$)	
	1/1 Cd_6Yb	$i\text{-CdYb}$
LDA calculation [Fig. 3(a)]	7.3	
LDA calculation [Fig. 3(b)]	7.4	
LDA + SO calculation [Fig. 3(c)]	11.8	
LDA + SO + U calculation [Fig. 3(d)]	6.1	
Experiment (Ref. 28)		19.2
Experiment (Ref. 29)		7
Experiment (Ref. 30)	51	7.5

at this photon energy the cross section of the Cd-4d states is the largest among all the states that may contribute in this binding energy range: For instance, the cross section of Cd-4d is one or two orders of magnitude larger than those of Cd-5s and Ca-4s.

The SO interaction and the strong electronic correlations in 1/1 Cd_6Yb are not only important for the peak structure

in the DOS, they are also essential for a proper description of the DOS near the Fermi energy. This is illustrated by a comparison of the electronic contributions to the specific heat,

$$\gamma = \frac{\pi^2}{3} k_B^2 \text{DOS}(E_F)(1 + \lambda), \quad (1)$$

calculated at various levels of sophistication (Table I), where we assumed that the phonon-correction factor $\lambda = 0$. (For a proper comparison with experiment λ can, of course, not be ignored.²⁸) Experimental values of γ are also given (Table I). It is remarkable³⁰ that γ is much lower in the QC than in the 1/1 approximant (Table I). This indicates a substantial rearrangement of states leading to a considerable lowering³⁰ of the DOS at the Fermi energy in $i\text{-CdYb}$. This rearrangement of states could be due purely to geometrical effects (Hume-Rothery), or geometrical effects coupled with increased hybridization between the Yb-5d states and the free-electronlike s and p states, a scenario that still remains to be explored.

In 1/1 Cd_6Yb the Yb-4f states are fully²⁸ occupied. The states at the Fermi energy have essentially no Yb-4f character.²⁸ Therefore, the Yb-4f states do not contribute²⁸ to transport properties or to the temperature dependence of thermodynamic properties. This is in clear contrast to the mixed-valent compound YbCuAl , in which the Yb-4f electrons are important for the heavy fermion character.³¹

In conclusion, the four Cd atoms inside the dodecahedral cavity occupied vertices of a (deformed) cube octahedron in the most stable model of 1/1 Cd_6Yb . The main features in the electronic DOS were insensitive to the model used. To get a good agreement with PE spectra it was necessary to include the SO interaction in the Hamiltonian, which is responsible for the splitting of the Cd-4d and the Yb-4f peaks in the DOS. In addition, the Cd-4d and Yb-4f electrons have strong correlations that cannot be treated in the LDA. We could describe these correlations with the LDA + U method by including a Hubbard-U term in the Hamiltonian for the Cd-4d and the Yb-4f states.

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